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Metal Complexes of Fluorophosphines. 4. Reactions of Mononuclear Metal Carbonyls with Methylaminobis(difluorophosphine)[1,2]

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Ultraviolet irradiation of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) with excess $CH_3N(PF_2)_2$ in diethyl ether results in complete displacement of all six carbonyl groups to give white volatile $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, W). Ultraviolet irradiation of $Fe(CO)_5$ with $CH_3N(PF_2)_2$ gives either yellow liquid $[CH_3N(PF_2)_2]_2FeCO$ or orange crystalline $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ depending upon the reaction conditions. Reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling tetrahydrofuran gives yellow crystalline $[CH_3N(PF_2)_2Fe(CO)_3]_2$ which readily loses carbon monoxide upon standing or heating in solution to form $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$. Reaction of $Fe_2(CO)_9$ with $CH_3N(PF_2)_2$ at room temperature gives a mixture of yellow liquid $CH_3N(PF_2)_2[Fe(CO)_4]_2$ and red-orange crystalline $CH_3N(PF_2)_2Fe_2(CO)_7$. Reactions of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ give white volatile insoluble $\{[CH_3N(PF_2)_2]_2Ni\}_n$, colorless crystalline $\{[CH_3N(PF_2)_2]_3Ni\}_2$, yellow $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$, and/or yellow $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ depending upon the reaction conditions. The carbonyl groups in $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ are readily replaced with a variety of ligands at room temperature even in the absence of ultraviolet irradiation to give complexes of the type $[CH_3N(PF_2)_2]_3Ni_2L_2$ (L = $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(C_6H_5)_3P$, monodentate $CH_3N(PF_2)_2$, and $(CH_3)_3CNC$).

Introduction

During the last two decades extensive chemistry of transition metals in low and even negative oxidation states has been developed using strong π-acceptor monodentate ligands such as carbon monoxide[4] and phosphorus trifluoride.[5] However, very little analogous low oxidation state metal chemistry has been developed using chelating strong π-acceptor ligands even though such ligands should form even more stable low oxidation state transition-metal derivatives because of the added stabilization from the chelate effect. The difficulty with such chemistry appears to be the introduction of strongly π-accepting donor groups into a structure capable of functioning as a chelate ligand. Thus, carbon monoxide cannot be incorporated into a polydentate ligand, and even the design of a multidentate chelating poly(isocyanide) poses difficulties because of the nearly linear hybridization of the isocyanide carbon atoms.

At the present time the most promising approach to a chelating strong π-acceptor ligand is the design of a poly(fluorophosphine) containing several RPF_2 donor units so situated that two or more of these trivalent phosphorus atoms can bond to a single metal atom. Unfortunately, most previously reported[6,7] methods of preparing trivalent phosphorus ligands containing PCH_2CH_2P structural units are not readily adapted to preparations of $F_2PCH_2CH_2PF_2$ and its homologues although Morse and Morse[8-10] have obtained such compounds by the addition of P_2F_4 to olefins. However, their preparative methods are not readily scaled up since they involve handling the unstable and not particularly readily prepared P_2F_4. Furthermore, published work[10] suggests that once obtained the RPF_2 derivatives (R = hydrocarbon group bonded through an sp^3 carbon such as methyl and ethyl as well as CH_2CH_2 bridges) are unstable themselves with respect to disproportionation to give the corresponding RPF_4 derivatives.

These considerations led us to consider other possible types of chelating poly(fluorophosphine) ligands without saturated hydrocarbon bridges between the donor phosphorus atoms. An attractive donor unit for such polydentate ligands is $RR'NPF_2$ since aminodifluorophosphines of this type are now well-known[11] to function as effective monodentate ligands in transition-metal chemistry. An already known class of potentially bidentate ligands containing this type of donor unit includes the alkylaminobis(diflurophosphines) $RN(PF_2)_2$ (R = CH_3,[12] C_2H_5,[12] C_6H_5[13]). Such bidentate ligands have already been shown[14] to form complexes of the type $C_2H_5N(PF_2)_2M(CO)_4$ (M = Cr, Mo, W). Furthermore, some ligands of the type $RN(PF_2)_2$ (e.g., R = CH_3, C_2H_5, C_6H_5) are readily accessible in quantities of 100 g or larger by reaction of the primary amine RNH_2 with excess phosphorus trichloride followed by fluorination.

This paper describes the reactions of the simple monometallic carbonyls $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$, and $Ni(CO)_4$ with the ligand $CH_3N(PF_2)_2$. In the cases of the metal hexacarbonyls pairwise substitution of all six carbonyl groups occurs under photochemical conditions thereby leading readily to the stable carbonyl-free complexes $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, W).[2a] Similar reactions of $Fe(CO)_5$ and $Ni(CO)_4$ with $CH_3N(PF_2)_2$ lead to a more complex variety of products including bimetallic derivatives where $CH_3N(PF_2)_2$ functions as a bridging rather than a chelating ligand. Details of these preparative studies, including the chemical and spectroscopic characterization of the products, are presented in this paper.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. (C, H, and N), and Galbraith Laboratories, Inc., Knoxville, Tenn. (P and F). Molecular weights were determined in benzene solutions using either a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia or a Perkin-Elmer Model 115 vapor pressure osmometer located in the laboratory of Professor R. Usón at the Departamento de Quimica Inorganica, Universidad de Zaragoza, Spain. Melting points were taken in capillaries and are uncorrected.

Infrared spectra were taken in KBr pellets or the indicated solvents and recorded on a Perkin-Elmer Model 257 or a Perkin-Elmer Model 621 spectrophotometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Mass spectra were taken at 70 eV on the University of Georgia Perkin-Elmer Hitachi RMU-6 mass spectrometer. Only the most intense ions are given along with their relative intensities in parentheses after the ion formula. Proton NMR spectra were recorded in $CDCl_3$ solutions on a Varian T-60 spectrometer at 60 MHz. Phosphorus-31 and carbon-13 NMR spectra were taken in CH_2Cl_2 or $CDCl_3$ solutions, respectively, and recorded at 40.3 and 25.0336 MHz, respectively, on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. The phosphorus-31 NMR chemical shifts are reported relative to external 85% H_3PO_4 with positive numbers denoting upfield chemical shifts. The phosphorus-31 NMR spectra of the complexes $CH_3N(PF_2)_2Fe_2(CO)_7$ and $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ like that of the free ligand[15] could be analyzed as X_2AAX_2 systems[16] whereas the resolution of the phosphorus-31 NMR spectra of the remaining complexes was only sufficient for simple first-order analyses as AX_2 or $AA'X_2$ systems. The carbon-13 chemical shifts (δ) are reported relative to internal tetramethylsilane with positive numbers indicating downfield chemical shifts. In order to allow observation of the carbon-13 resonances of the metal carbonyl groups, chromium (III) acetylacetonate was used as a shiftless relaxation reagent.[17]

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling air-sensitive organometallic compounds, particularly in solution; and (c) filling evacuated vessels containing potentially air-sensitive materials. Ultraviolet irradiations were performed using an immersion Englehard-Hanovia 450-W mercury ultraviolet lamp with a water-cooled Pyrex jacket. Tetrahydrofuran and diethyl ether were freshly distilled over $LiAlH_4$ or CaH_2.

The metal carbonyls $M(CO)_6$ (M = Cr, Mo, W: Pressure Chemical Co., Pittsburgh, Pa.), $Fe(CO)_5$ (GAF Corp., New York, N.Y.), and $Ni(CO)_4$ (Matheson Co., Morrow, Ga.) were purchased from the indicated sources. The metal carbonyls $Fe_2(CO)_9$[18] and $Fe_3(CO)_{12}$[19] were prepared by the cited published procedures.

Preparation of $CH_3N(PF_2)_2$. The preparation reported by Nixon[12] was scaled up considerably to provide the large quantities of $CH_3N(PF_2)_2$ required for this and related research using the methods described below.

(a) Preparation of $CH_3N(PCl_2)_2$. A mixture of 85 g (1.25 mol) of methylamine hydrochloride (dried overnight at 100 °C (0.1 mm)), 420 mL (661 g, 4.81 mol) of phosphorus trichloride, and 500 mL of 1,1,2,2-tetrachloroethane was boiled under reflux with magnetic stirring for 10 days. Excess phosphorus trichloride and tetrachloroethane were removed by distillation at atmospheric pressure. Vacuum distillation of the residue gave 245 g (84% yield) of $CH_3N(PCl_2)_2$, bp 80–90 °C (0.3 mm).

(b) Preparation of $CH_3N(PF_2)_2$. A mixture of 245 g (1.05 mol) of $CH_3N(PCl_2)_2$, 350 g (1.53 mol) of antimony trifluoride (purchased from Ozark-Mahoning Corp., Tulsa, Okla.), and 500 mL of methylcyclohexane was warmed gently with a heat gun under an efficient reflux condenser topped with a –78 °C condenser. After the reaction started, gentle reflux was maintained for 1 h. Distillation of the resulting mixture at atmospheric pressure gave 133 g (76% yield) of $CH_3N(PF_2)_2$: bp 45 °C (lit.[12] bp 40–42 °C); phosphorus-31 NMR δ –140.8, $|^1J(PF)| = 1264$ Hz, $|^3J(PF)| = 44$ Hz, $|^2J(PP)| = 442$ Hz (lit.[15] δ –141.5, $|^1J(PF)| = 1264$ Hz, $|^3J(PF)| = 47$ Hz, $|^2J(PP)| = 437$ Hz).

Preparation of $[CH_3N(PF_2)_2]_3Cr$. A mixture of 2.20 g (10 mmol) of $Cr(CO)_6$, 8.40 g (50.3 mmol) of $CH_3N(PF_2)_2$, and 250 mL of diethyl ether was exposed to the ultraviolet irradiation from the immersion lamp for 22 h. Filtration of the resulting reaction solution through Celite followed by evaporation and washing with cold pentane gave 3.02 g (55% yield) of $[CH_3N(PF_2)_2]_3Cr$. Sublimation at 90 °C (0.1 mm) gave the analytical sample: mp 182–183 °C; IR (KBr) 2955 (vw), 1173 (m), 831 (s), 788 (w), 673 (m) cm^{-1}; proton NMR ($CDCl_3$) τ 7.27; carbon-13 NMR ($CDCl_3$) δ 29.3; phosphorus-31 NMR (CH_2Cl_2) δ –180.3 ($|^1J(PF)| = 1250$ Hz); mass spectrum $[CH_3N(PF_2)_2]_3Cr^+$ (23), $[CH_3N(PF_2)_2]_2Cr^+$ (36), $CH_3N(PF_2)_2CrF^+$ (13), $CH_3N(PF_2)_2Cr^+$ (100). Anal. Calcd for $C_3H_9CrF_{12}N_3P_6$: C, 6.5; H, 1.6; F, 41.2; N, 7.6, P, 33.6; mol wt 553. Found: C, 6.6; H, 1.9; F, 42.0; N, 7.7; P, 34.4; mol wt 498.

Preparation of $[CH_3N(PF_2)_2]_3Mo$. A mixture of 1.31 g (5 mmol) of $Mo(CO)_6$, 5.0 g (30 mmol) of $CH_3N(PF_2)_2$, and 250 mL of diethyl ether was exposed to the ultraviolet irradiation from the immersion lamp for 18 h. Evaporation of solvent from the filtered solution and cooling gave 1.67 g (56% yield) of white $[CH_3N(PF_2)_2]_3Mo$. Sublimation at 70–80 °C (0.1 mm) gave the analytical sample: mp 216–218 °C; IR (KBr) 2965 (vw), 1173 (s), 835 (vs), 800 (s), 665 (m) cm^{-1}; proton NMR ($CDCl_3$) τ 7.31; carbon-13 NMR ($CDCl_3$) δ 28.7; phosphorus-31 NMR (tetrahydrofuran) δ –157.6 ($[^1J(PF)| = 1220$ Hz); mass spectrum $[CH_3N(PF_2)_2]_3Mo^+$ (100), $[CH_3N(PF_2)_2]_2MoF^+$ (10), $[CH_3N(PF_2)_2]_2Mo^+$ (20), $CH_3N(PF_2)_2Mo^+$ (60), $CH_3NPF_2Mo^+$ (25). Anal. Calcd for $C_3H_9F_{12}MoN_3P_6$: C, 6.0; H, 1.5; F, 38.2; N, 7.0; P, 31.1; mol wt 597. Found: C, 6.2; H, 1.6; F, 37.9; N, 7.1; P, 31.1; mol wt 605.

Preparation of $[CH_3N(PF_2)_2]_3W$. A mixture of 1.76 g (5 mmol) of $W(CO)_6$, 4.86 g (29 mmol) of $CH_3N(PF_2)_2$, and 250 mL of diethyl ether was exposed to ultraviolet irradiation from the immersion lamp for 56 h. Evaporation of solvent from the filtered solution and treatment with cold pentane gave 1.58 g (46% yield) of slightly yellowish $[CH_3N(PF_2)_2]_3W$. Sublimation at 90–100 °C (0.1 mm) gave the white analytical sample: mp 221–223 °C; IR (KBr) 2970 (vw), 1178 (s), 865 (sh), 838 (vs), 802 (m), 670 (w) cm^{-1}; proton NMR ($CDCl_3$) τ 7.33; carbon-13 NMR ($CDCl_3$) δ 29.9; phosphorus-31 NMR (acetone) δ –125.2 ($|^1J(PF)| = 1226$ Hz); mass spectrum $[CH_3N(PF_2)_2]_3W^+$ (100), $[CH_3N(PF_2)_2]_2WF^+$ (12), $CH_3N(PF_2)_2W^+$ (94). Anal. Calcd for $C_3H_9F_{12}N_3P_6W$: C, 5.3; H, 1.3; F, 33.3; N, 6.1; P, 27.1; mol wt 685. Found: C, 5.2; H, 1.3; F, 33.0; N, 6.1; P, 27.3; mol wt 691.

Preparation of $[CH_3N(PF_2)_2]_2FeCO$. A mixture of 1.55 g (8 mmol) of $Fe(CO)_5$, 5.26 g (31.5 mmol) of $CH_3N(PF_2)_2$, and 300 mL of tetrahydrofuran was exposed to the ultraviolet irradiation from the immersion lamp for 5 h. Solvent was then removed from the reaction mixture of 25 °C (25 mm). A hexane solution of the oily residue was chromatographed on a 1.5 × 30 cm Florisil column. Elution of the yellow band with hexane gave a yellow liquid. Evaporative distillation of this liquid at 80 °C (0.3 mm) gave 1.65 g (49% yield) of yellow liquid $[CH_3N(PF_2)_2]_2FeCO$: IR (hexane) ν(CO) 1990 cm^{-1}; proton NMR ($CDCl_3$) τ 7.38 (apparent triplet, $J = 12$ Hz); phosphorus-31 NMR (CH_2Cl_2) δ –151.0 ($|^1J(PF)| = 1250$ Hz). Anal. Calcd for $C_3H_6F_8FeNP_4O$: C, 8.6; H, 1.6; F, 36.4; N, 6.7; P, 29.7. Found: C, 8.5; H, 1.6; F, 34.6; N, 6.9; P, 28.1.

Preparation of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ from $Fe(CO)_5$. A mixture of 1.95 g (10 mmol) of $Fe(CO)_5$, 1.67 g (10 mmol) of $CH_3N(PF_2)_2$, and 250 mL of degassed pentane was exposed to the ultraviolet irradiation from the immersion lamp for 90 min. The resulting orange-yellow precipitate was filtered and washed with pentane to give 1.14 g (39% yield) of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$. A low-temperature crystallization of this product from a mixture of dichloromethane and hexane gave the orange crystalline analytical sample: mp 192–193 °C; IR (hexane) ν(CO) 2066 (m), 2026 (s), 1992 (s), 1978 (m), 1786 (m) cm^{-1}; phosphorus-31 NMR (acetone) δ –187.1 (broad triplet, $J \approx 1140 \pm 100$ Hz). Anal. Calcd for $C_7H_6F_8Fe_2N_2O_5P_4$: C, 14.3; H, 1.0; F, 25.9; N, 4.8; P, 21.1. Found: C, 14.4; H, 1.1; F, 25.8; N, 4.8; P, 21.2.

Similar results were obtained by carrying out the ultraviolet irradiation of $Fe(CO)_5$ and $CH_3N(PF_2)_2$ in a 1:1 molar ratio in diethyl ether rather than pentane solution. However, in this case the $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ did not precipitate spontaneously from the reaction mixture. Instead it was isolated by evaporation of the solvent followed by chromatography on Florisil using a mixture of hexane and dichloromethane for the eluent.

Reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in Tetrahydrofuran. A mixture of 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$, 1.20 g (7.2 mmol) of $CH_3N(PF_2)_2$, and 100 mL of tetrahydrofuran was stirred at room temperature overnight and then boiled under reflux for 1 h. Solvent was then removed at ~25 °C (25 mm). The yellow crystalline solid was crystallized from a mixture of dichloromethane and hexane by slow evaporation to give 0.42 g (23% yield) of yellow $[CH_3N(PF_2)_2Fe(CO)_3]_2$: mp 128–129 °C; IR in (dichloromethane) ν(CO) 2040 (w), 2037 (w), 2033 (m), 2011 (s), 2005 (s), 1974 (s) cm^{-1}. Anal. Calcd for $C_8H_6F_8Fe_2N_2O_6P_4$: C, 15.7; H, 1.0; F, 24.8; N, 4.6; P, 20.2; mol wt 614. Found: C, 15.7; H, 1.0; F, 24.5; N, 4.6; P, 19.5; mol wt 591.

Chromatography of the filtrates from the crystallization of $[CH_3N(PF_2)_2Fe(CO)_3]_2$ on Florisil followed by elution of the resulting orange-yellow band with 1:1 dichloromethane–hexane and evaporation of the eluate gave 0.43 g (25% yield) of orange $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ identified by elemental analyses and comparison of its infrared spectrum in the ν(CO) region with that of material prepared from $Fe(CO)_5$ and $CH_3N(PF_2)_2$ as described above.

Reaction or $Fe_2(CO)_9$ with $CH_3N(PF_2)_2$. A mixture of 10.9 g (30 mmol) of $Fe_2(CO)_9$, 5.0 g (30 mmol) of $CH_3N(PF_2)_2$, and 200 mL of diethyl ether was stirred at room temperature for 3 h. The $Fe_2(CO)_9$ dissolved with gas evolution to form a red-orange solution. Solvent was removed from this solution at ~25 °C (35 mm). The residue was chromatographed on a Florisil column in hexane solution. Elution of the first yellow band with hexane gave 3.8 g (25% yield on the basis of $Fe_2(CO)_9$) of yellow liquid $CH_3N(PF_2)_2[Fe(CO)_4]_2$: IR (hexane) ν(CO) 2090 (m), 2023 (s), 2017 (s), 1996 (s), 1985 (s), 1976 (s) cm^{-1}; proton NMR ($CDCl_3$) τ 7.13 (doublet, $J = 12$ Hz), τ 7.23 (doublet, $J = 12$ Hz); carbon-13 NMR ($CDCl_3$) δ 211.1, 210.4, 209.7, 34.2, 27.6; phosphorus-31 NMR (CH_2Cl_2) δ –197.6 (triplet, $J = 1203$ Hz) and δ 194.2 ($J = 1150$ Hz). The analytical sample was purified by repeated evaporative distillation at 45 °C (0.05 mm) but was never obtained completely pure. Anal. Calcd for $C_9H_3F_4Fe_2NO_8P_2$: C, 21.5; H, 0.6; N, 2.8; mol wt 503. Found: C, 22.6; H, 0.8; N, 3.4; mol wt 490.

After elution of the $CH_3N(PF_2)_2[Fe(CO)_4]_2$ the chromatogram was eluted with a 1:1 mixture of dichloromethane and hexane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.37 g (2.6% yield) of red-orange crystalline $CH_3N(PF_2)_2Fe_2(CO)_7$: mp 75–77 °C; IR (pentane) ν(CO) 2090 (m), 2040 (s), 2025 (s), 2000 (s), 1995 (vs), 1982 (m), 1805 (s) cm^{-1}; proton NMR ($CDCl_3$) τ 7.00 (triplet, $J = 7$ Hz); carbon-13 NMR ($CDCl_3$) δ 215.2, 30.7; phosphorus-31 NMR (CH_2Cl_2) δ −186.4 (X_2AAX_2 pattern: $|^1J(PP)| = 1190$ Hz, $|^3J(PF)| = 16$ Hz, $|^2J(PP)| = 283$ Hz). Anal. Calcd for $C_8H_3F_4Fe_2NO_7P_2$: C, 20.2; H, 0.6; F, 16.0; N, 2.9; P, 13.0; mol wt 475. Found: C, 20.3; H, 0.7; F, 16.2; N, 3.1; P, 13.2; mol wt 490.

In other similar experiments on a smaller scale and on solutions 2 or 3 times more dilute the yield of $CH_3N(PF_2)_2Fe_2(CO)_7$ from equimolar quantities of $Fe_2(CO)_9$ and $CH_3N(PF_2)_2$ rose to 4–5% based on total $Fe_2(CO)_9$ introduced.

Reactions of $Ni(CO)_4$ with $CH_3N(PF_2)_2$. (a) Photochemical Reaction with Excess Ligand. A solution of 1.17 g (7 mmol) of $Ni(CO)_4$, 3.0 g (18 mmol) of $CH_3N(PF_2)_2$, and 400 mL of diethyl ether was exposed for 3 h to the ultraviolet irradiation from the immersion lamp using a −78 °C condenser to ensure retention of the toxic and volatile $Ni(CO)_4$ in the reaction mixture. Removal of diethyl ether from the reaction mixture gave a liquid which exhibited a single infrared ν(CO) band at ~2050 cm^{-1}. Heating this liquid at ~150 °C (0.4 mm) did not result in distillation but instead in solidification to give 1.6 g (58% yield) of white solid $\{[CH_3N(PF_2)_2]_2Ni\}_n$. This solid gave a light yellow sublimate, mp 211–213 °C, when heated at 210 °C (0.4 mm) and was insoluble or very sparingly soluble in dichloromethane, chloroform, and acetone; infrared spectrum in KBr: 2965 (vw), 1467 (vw, br), 1210 (vw, sh), 1189 (w), 1103 (vw, sh), 1045 (m), 947 (w), 865 (s), 809 (s), 684 (m) cm^{-1}; mass spectrum $[CH_3N(PF_2)_2]_4Ni_2^+$ (11), $[CH_3N(PF_2)_2]_3Ni_2^+$ (62), $[CH_3N(PF_2)_2]_2Ni_2^+$ (100), $CH_3N(PF_2)_2Ni_2PF_2NCH_3^+$ (19), $CH_3N(PF_2)_2Ni_2PFNCH_3^+$ (26), $[CH_3N(PF_2)_2]_2Ni_2F^+$ (45), $CH_3N(PF_2)_2Ni^+$ (68). Because of the very limited solubility of this compound neither its NMR spectra nor its molecular weight in solution could be determined. Anal. Calcd for $C_2H_6F_8N_2NiP_4$: C, 6.1; H, 1.5; N, 7.1. Found: C, 6.1, 6.1; H, 1.6, 1.5; N, 7.2, 7.2.

(b) Isolation of the Intermediate from the Photochemical Reaction. A mixture of 1.0 g (6 mmol) of $Ni(CO)_4$, 4.0 g (24 mmol) of $CH_3N(PF_2)_2$, and 400 mL of diethyl ether was exposed for 3 h to the ultraviolet irradiation from the immersion lamp. Solvent was then removed from the reaction mixture at ~25 °C (25 mm). The residue was purified by low-temperature (−78 °C) crystallization from pentane. Material prepared by this method melted at or near room temperature but heating this product at 100 °C (0.1 mm) gave 0.5 g (15% yield) of colorless crystals of $[CH_3N(PF_2)_2]_6Ni_2$, mp 83–85 °C, which were soluble in organic solvents: proton NMR ($CDCl_3$) τ 7.04 (broad, $W_{1/2} \approx 16$ Hz); carbon-13 NMR ($CDCl_3$) δ 26.9 and 24.3 of relative heights 31:37; phosphorus-31 NMR ($CDCl_3$) δ −151.7 ($|^1J(PF)| \approx 1250$ Hz), δ −137.3 ($|^1J(PF)| = 1270$ Hz, $|^2J(PP)| = 265$ Hz). Anal. Calcd for $C_6H_{18}F_{24}N_6Ni_2P_{12}$: C, 6.4; H, 1.6; N, 7.5; mol wt 1119.4. Found: C, 6.7; H, 1.6; N, 7.7; mol wt 1190.

A similar product was isolated from the reaction of 0.85 g (5 mmol) of $Ni(CO)_4$ with 3.25 g (19 mmol) of $CH_3N(PF_2)_2$ in 100 mL of boiling hexane for 3 h.

(c) Photochemical Reaction of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ in a 2:3 Molar Ratio. A mixture of 2.77 g (16.2 mmol) of $Ni(CO)_4$, 4.0 g (24 mmol) of $CH_3N(PF_2)_2$, and 300 mL of diethyl ether was stirred for 30 min at room temperature and then exposed to the ultraviolet irradiation from the immersion lamp until evolution of CO ceased (~1 h). Solvent was removed from the reaction mixture at ~25 °C (35 mm). During this process the originally colorless solution became yellow. Low-temperature crystallization of the residue from pentane or hexane gave 3.30 g (60% yield) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$. A second low-temperature crystallization from pentane gave the analytical sample as yellow needles: mp 98–100 °C; IR (hexane) ν(CO) 2070 (s), 2055 (s) cm^{-1}; proton NMR ($CDCl_3$) τ 6.95 (broad, $W_{1/2} \approx 12$ Hz); carbon-13 NMR ($CDCl_3$) δ 189.2, 26.4; phosphorus-31 NMR ($CDCl_3$) δ −153.9 (broad triplet: $J \approx 1130 \pm 100$ Hz); mass spectrum (chamber temperature 135 °C, sample temperature 80 °C) $[CH_3N(PF_2)_2]_4Ni_2^+$ (10), $[CH_3N(PF_2)_2]_3Ni_2^+$ (57), $[CH_3N(PF_2)_2]_2Ni_2^+$ (100), $CH_3N(PF_2)_2Ni_2PF_2NCH_3^+$ (19), $CH_3N(PF_2)_2Ni_2PFNCH_3^+$ (30), $CH_3N(PF_2)_2Ni_2F^+$ (38), $CH_3N(PF_2)_2Ni^+$ (38). Anal. Calcd for $C_5H_9F_{12}N_3Ni_2O_2P_6$: C, 8.9; H, 1.3; N, 6.2; mol wt 674.4. Found: C, 8.8; H, 1.5; N, 6.6; mol wt 689.

The same product was also obtained in similar yield by allowing $Ni(CO)_4$ and $CH_3N(PF_2)_2$ to react under similar conditions in a 1:1 rather than 2:3 molar ratio.

(d) Thermal Reaction with Equimolar Quantities of $Ni(CO)_4$ and $CH_3N(PF_2)_2$. A mixture of 2.41 g (14.1 mmol) of $Ni(CO)_4$, 2.33 g (14.0 mmol) of $CH_3N(PF_2)_2$, and 100 mL of hexane was boiled under reflux for 1 h using a −78 °C condenser. The reaction mixture successively became light yellow, yellow, light red, red, and finally dark yellow with some evidence for decomposition and with continual evolution of carbon monoxide. The reaction mixture was filtered through Celite. Hexane was removed at ~25 °C (25 mm). The resulting yellow oil was purified by low-temperature crystallization from pentane to give 2.02 g (53% yield) of yellow needles of $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$: mp 55–57 °C; IR (hexane) ν(CO) 2070 (s), 2055 (s), 1891 (s) cm^{-1}; proton NMR ($CDCl_3$) τ 7.05 (triplet, $J = 6$ Hz); carbon-13 NMR ($CDCl_3/CS_2$) δ 221.6 (broad), 26.7; phosphorus-31 NMR (CH_2Cl_2) δ −152.9 (X_2AAX_2 pattern: $|^1J(PF)| = 1238$ Hz, $|^3J(PF)| = 54$ Hz, $|^2J(PP)| = 537$ Hz). Anal. Calcd for $C_5H_6F_8N_2Ni_2O_3$: C, 11.2; H, 1.1; N, 5.2; mol wt 535.4. Found: C, 11.1, 11.1; H, 1.2, 1.2; N, 5.4, 5.3; mol wt 511.

Reactions of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$. (a) With Trimethyl Phosphite. A solution of 0.48 g (0.71 mmol) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ in 100 mL of hexane was treated with 0.6 mL (0.63 g, 5.1 mmol) of trimethyl phosphite at room temperature. Immediate CO evolution occurred. The reaction mixture was stirred for 30 min at room temperature and then boiled under reflux for an additional 30 min. Removal of solvent at ~25 °C (25 mm) followed by crystallization of the residue from a mixture of dichloromethane and hexane gave 0.54 g (88% yield) of white crystalline $[CH_3N(PF_2)_2]_3Ni_2[P(OCH_3)_3]_2$: mp 191–193 °C; proton NMR ($CDCl_3$) τ 6.38 (doublet, $J = 10$ Hz) and τ 7.05 (broad singlet) of approximate relative intensities 18:9 corresponding to the OCH_3 and NCH_3 protons, respectively; carbon-13 NMR ($CDCl_3$) δ 50.6 and 26.4 (broad) corresponding to the OCH_3 and NCH_3 carbons, respectively. Anal. Calcd for $C_9H_{27}F_{12}N_3Ni_2O_6P_8$: C, 12.5; H, 3.1; N, 4.8. Found: C, 12.5; H, 3.1; N, 4.9.

(b) With Triethyl Phosphite. A solution of 0.50 g (0.74 mmol) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ in 50 mL of hexane was treated with 1.04 mL (1.00 g, 6 mmol) of triethyl phosphite at room temperature. Isolation of product by a procedure completely analogous to that given above for the preparation of $[CH_3N(PF_2)_2]_3Ni_2[P(OCH_3)_3]_2$ gave 0.59 g (84% yield) of white crystalline $[CH_3N(PF_2)_2]_3Ni_2[P(OC_2H_5)_3]_2$: mp 181–183 °C; proton NMR ($CDCl_3$) τ 6.08 (multiplet), 7.1 (broad singlet), and 8.89 (triplet, $J = 7$ Hz) of approximate relative intensities 12:9:18 corresponding to the ethyl CH_2, the NCH_3, and the ethyl CH_3 protons, respectively; carbon-13 NMR ($CDCl_3$) δ 59.4, 26.2 (broad), and 16.2 corresponding to the OCH_2, NCH_3, and ethyl CH_3 carbons, respectively. Anal. Calcd for $C_{15}H_{39}F_{12}N_3Ni_2O_6P_8$: C, 18.9; H, 4.1; N, 4.4; mol wt 950.4. Found: C, 19.0; H, 4.1; N, 4.4; mol wt 953.

(c) With Triphenylphosphine. A solution of 0.60 g (0.89 mmol) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ in 70 mL of hexane was treated with 0.52 g (2 mmol) of triphenylphosphine. Immediate gas evolution occurred with the concurrent formation of a precipitate. After the solution was boiled under reflux for 15 min, the precipitate was filtered, washed with hot hexane, and dried to give 0.9 g (89% yield) of light yellow $[CH_3N(PF_2)_2]_3Ni_2[P(C_6H_5)_3]_2$: mp 270 °C dec; proton NMR ($CDCl_3$) τ 2.65 (multiplet) and 7.25 (broad) of approximate relative intensities 30:9 corresponding to the C_6H_5 and CH_3N protons, respectively. Anal. Calcd for $C_{39}H_{39}F_{12}N_3Ni_2P_8$: C, 41.0; H, 3.4; N, 3.7. Found: C, 40.7; H, 3.4; N, 3.8.

(d) With *tert*-Butyl Isocyanide. A solution of 0.59 g (0.87 mmol) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ in 70 mL of hexane was treated with 0.5 mL (0.38 g, 4.6 mmol) of *tert*-butyl isocyanide.[20] Immediate CO evolution occurred. After the solution was stirred for 30 min at room temperature, evaporation of the hexane and removal of the product by filtration gave 0.33 g (48% yield) of $[CH_3N(PF_2)_2]_3Ni_2[CNC(CH_3)_3]_2$. Recrystallization from pentane gave the white analytical sample: mp 173–175 °C; proton NMR ($CDCl_3$) τ 7.09 (broad singlet) and 8.55 (singlet) of approximate relative intensities 9:18 corresponding to the methyl protons of the $(CH_3)_3CNC$ and $CH_3N(PF_2)_2$ ligands, respectively; carbon-13 NMR ($CDCl_3$) δ 148.0 (very weak, broad), 56.5, 30.2, 25.5. Anal. Calcd for $C_{13}H_{27}F_{12}N_5Ni_2P_6$: C, 19.9; H, 3.4; N, 8.9; mol wt 784.4. Found: C, 20.0; H, 3.4; N, 8.9; mol wt 779.

(e) With $CH_3N(PF_2)_2$. A mixture of 1.0 g (1.5 mmol) of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$, 0.8 g (4.8 mmol) of $CH_3N(PF_2)_2$, and 70 mL of hexane was stirred for 30 h at room temperature. Partial removal of hexane in a nitrogen stream followed by cooling to −78

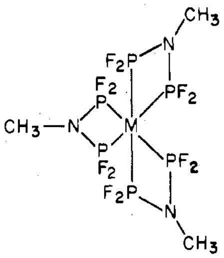
°C led to the crystallization of 1.07 g (75% yield) of $[CH_3N(PF_2)_2]_5Ni_2$. Low-temperature recrystallization of this product from pentane gave the analytical sample: mp 88–90 °C; proton NMR ($CDCl_3$) τ 7.1 (broad singlet); carbon-13 NMR ($CDCl_3$) δ 26.8, 24.0. Anal. Calcd for $C_5H_{15}F_{20}N_5Ni_2P_{10}$: C, 6.3; H, 1.6; N, 7.3. Found: C, 6.4; H, 1.8; N, 7.6.

Reactions of $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ with Trialkyl Phosphites. (a) Trimethyl Phosphite. Reaction of 0.5 g (0.93 mmol) of $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ with 0.6 mL (0.63 g, 5.1 mmol) of trimethyl phosphite in 70 mL of boiling hexane for 16 h gave 0.25 g (47% yield on the basis of $CH_3N(PF_2)_2$ ligands) of $[CH_3N(PF_2)_2]_3Ni_2[P(OCH_3)_3]_2$, mp 190–192 °C, after low-temperature crystallization from hexane.

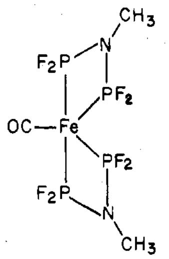
(b) Triethyl Phosphite. Reaction of 1.13 g (2.1 mmol) of $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ with 2.08 mL (2.00 g, 12.1 mmol) of triethyl phosphite in 70 mL of boiling hexane for 20 h gave 0.44 g (33% yield on the basis of $CH_3N(PF_2)_2$ ligands) of $[CH_3N(PF_2)_2]_3Ni_2[P(OC_2H_5)_3]_2$, mp 183–185 °C, after low-temperature crystallization from hexane.

Results

(1) Chromium, Molybdenum, and Tungsten Derivatives. Ultraviolet irradiation of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) with $CH_3N(PF_2)_2$ readily substitutes all six carbonyl groups to give the corresponding $[CH_3N(PF_2)_2]_3M$ derivatives. These products, like the metal hexacarbonyls $M(CO)_6$ and the trifluorophosphine complexes[21] $M(PF_3)_6$, are white volatile relatively air-stable solids. The chromium compound $[CH_3N(PF_2)_2]_3Cr$ can even be distilled unchanged at ~256 °C (1 atm) in a capillary. The infrared and NMR spectra (proton, carbon-13, and phosphorus-31) of the $[CH_3N(PF_2)_2]_3M$ complexes are all consistent with their formulation as the zerovalent tris(bidentate) chelates I (M = Cr, Mo, W). Thus, the infrared spectra of the $[CH_3N(PF_2)_2]_3M$ complexes exhibit the expected strong ν(P–F) frequencies at 831–838 cm^{-1}. The proton and carbon-13 NMR spectra each exhibit a single resonance owing to the three equivalent methyl groups. Similarly the phosphorus-31 NMR spectra exhibit a single broad triplet suggesting equivalence of all six phosphorus atoms and inability to resolve the longer range $|(^2J(PP)|$ and $|^3J(PF)|$ couplings. The mass spectra of the $[CH_3N(PF_2)_2]_3M$ complexes all exhibit intense molecular ions and the fragment ions $CH_3N(PF_2)_2M^+$. The relative abundances of the $[CH_3N(PF_2)_2]_2M^+$ ions in the mass spectra of the $[CH_3N(PF_2)_2]_3M$ complexes decrease rather markedly upon increase in the atomic number of M apparently at the expense of $[CH_3N(PF_2)_2]_2MF^+$.



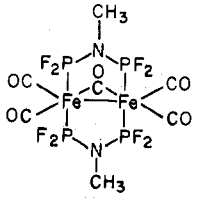
I



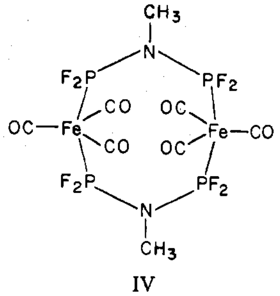
II

(2) Iron Derivatives. Since $Fe(CO)_5$ has an odd number of carbonyl groups, it is not possible to replace all of its carbonyl groups with bidentate $CH_3N(PF_2)_2$ ligands to form a monometallic zerovalent $[CH_3N(PF_2)_2]_n$ Fe complex with the favored 18-electron configuration of the next rare gas.[22,23] Ultraviolet irradiation of $Fe(CO)_5$ with excess $CH_3N(PF_2)_2$ in the polar solvent tetrahydrofuran was found to give the monocarbonyl $[CH_3N(PF_2)_2]_2FeCO$ as a yellow volatile liquid. The spectroscopic data are consistent with structure II for this complex. The relatively high position for an L_4FeCO derivative of the single ν(CO) frequency at 1990 cm^{-1} confirms the expected high π-acceptor properties of the phosphorus atoms in $CH_3N(PF_2)_2$.

Ultraviolet irradiation of equimolar quantities of $Fe(CO)_5$ with $CH_3N(PF_2)_2$ in a less polar solvent than the strong donor tetrahydrofuran such as diethyl ether or pentane does not give $[CH_3N(PF_2)_2]_2FeCO$ (II) as the major product. Instead, an orange crystalline bimetallic complex $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ is obtained. Structure III for this complex has been confirmed by X-ray crystallography.[2b] A characteristic feature of this structure is the metal–metal bond bridged by two $CH_3N(PF_2)_2$ ligands and one carbonyl group. The bridging carbonyl group in structure III leads to an infrared ν(CO) frequency at 1786 cm^{-1} in addition to the expected four ν(CO) frequencies in the range 2066–1978 cm^{-1} arising from the four terminal carbonyl groups.



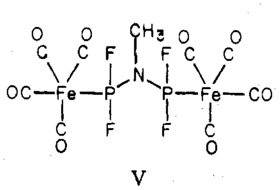
III



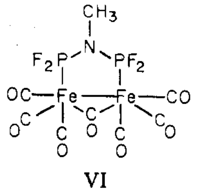
IV

Reactions of $CH_3N(PF_2)_2$ were also investigated with the polynuclear iron carbonyls $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ which are more reactive than $Fe(CO)_5$. Thermal reactions of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling tetrahydrofuran result in rupture of the iron triangle to give ultimately the orange bimetallic product $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (III) mentioned above. If the reaction in boiling tetrahydrofuran is conducted for a short time, a second bimetallic product, yellow $[CH_3N(PF_2)_2Fe(CO)_3]_2$, is isolated. This yellow product has been shown by X-ray crystallography[2b] to have the structure IV containing two nearly square-pyramidal iron atoms in contrast to the usual trigonal-bipyramidal iron atoms found in five-coordinate iron(0) complexes. Formation of the bimetallic complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (IV) instead of the still unknown monometallic complex $CH_3N(PF_2)_2Fe(CO)_3$ suggests some difficulty for the very small bite bidentate $CH_3N(PF_2)_2$ ligand to span adjacent coordination positions in some five-coordinate complexes. Dimerization of $CH_3N(PF_2)_2Fe(CO)_3$ to $[CH_3N(PF_2)_2Fe(CO)_3]_2$, thereby converting the four-membered ring of a biligate monometallic $CH_3N(PF_2)_2$ ligand to a larger ring of a biligate bimetallic $CH_3N(PF_2)_2$ ligand, relieves some steric strain. The diiron hexacarbonyl derivative $[CH_3N(PF_2)Fe(CO)_3]_2$ (IV) itself is also unstable under certain conditions. In solution it loses carbon monoxide to form the diiron pentacarbonyl derivative $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (III).

The iron carbonyl $Fe_2(CO)_9$ is normally still more reactive than $Fe_3(CO)_{12}$ since $Fe_2(CO)_9$ dissociates into unreactive $Fe(CO)_5$ and reactive $Fe(CO)_4$ units at or near room temperature. Treatment of $Fe_2(CO)_9$ with $CH_3N(PF_2)_2$ at room temperature was found to give two products. One product is a yellow liquid of stoichiometry $CH_3N(PF_2)_2[Fe(CO)_4]_2$ and presumed structure V. This compound could not be obtained completely pure. Furthermore, the presence of two phosphorus-31 triplets in the most highly purified samples suggest a mixture of stereoisomers possibly involving apical vs. equatorial monosubstitution.



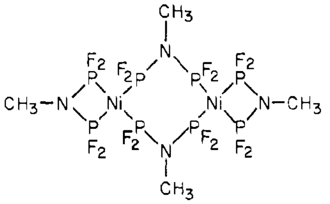
V



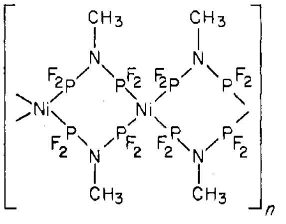
VI

The second product from the reaction of $Fe_2(CO)_9$ and $CH_3N(PF_2)_2$, normally formed in much smaller yield than V, is red-orange crystalline $CH_3N(PF_2)_2Fe_2(CO)_7$ of apparent structure VI. In VI the bridging carbonyl group exhibits a characteristic $\nu(CO)$ frequency at 1805 cm^{-1} in addition to six $\nu(CO)$ frequencies in the range 2090–1982 cm^{-1} for the six terminal carbonyl groups. The phosphorus-31 NMR spectrum of $CH_3N(PF_2)_2Fe_2(CO)_7$ (VI) exhibits a clear X_2AAX_2 pattern like the free ligand $CH_3N(PF_2)_2$; from the spectrum of VI meaningful values for the three major coupling constants $|^1J(PF)|$, $|^3J(PF)|$, and $|^2J(PP)|$ can be derived. This contrasts with the phosphorus-31 NMR spectrum of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (III) where the peaks are too broad for such detailed analysis and even a reasonably accurate estimate for $|^1J(PF)|$ cannot be obtained. Reaction of $[(C_6H_5)_2P]_2CH_2$ with $Fe_2(CO)_9$ has been reported[24] to give a diiron heptacarbonyl complex $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ shown by X-ray crystallography to have a structure similar to structure VI proposed for $CH_3N(PF_2)_2Fe_2(CO)_7$.

(3) Nickel Derivatives. If the ligand $CH_3N(PF_2)_2$ replaces all carbonyl groups in $Ni(CO)_4$ similar to its replacement of all six carbonyl groups in $Cr(CO)_6$ to form $[CH_3N(PF_2)_2]_3Cr$, the resulting product should be a volatile monometallic complex $[CH_3N(PF_2)_2]_2Ni$. Ultraviolet irradiation of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ was found to give a liquid which upon attempted vacuum distillation solidifies to give a product of composition $\{[CH_3N(PF_2)_2]_2Ni\}_n$. The insolubility of $\{[CH_3N(PF_2)_2]_2Ni\}_n$ in organic solvents and its volatility only at ~200 °C (0.4 mm) as contrasted with the solubility of $[CH_3N(PF_2)_2]_3Cr$ in organic solvents and its volatility even at 90 °C (0.1 mm) precludes formulation of the nickel complex as the mononuclear $[CH_3N(PF_2)_2]_2Ni$. The mass spectrum of $\{[CH_3N(PF_2)_2]Ni\}_n$ vapor exhibits high abundances of the binuclear ions $[CH_3N(PF_2)_2]_nNi_2^+$ (n = 4, 3, 2) suggesting that this complex vaporizes as the dimer $[CH_3N(PF_2)_2]_4Ni_2$, possibly with structure VII containing two biligate bimetallic ("bridging") and two biligate monometallic ("terminal") $CH_3N(PF_2)_2$ ligands. However, the insolubility of solid $\{[CH_3N(PF_2)_2]_2Ni\}_n$ suggests that in the solid state this complex is a coordination polymer of the type VIII which forms reversibly the dimer VII on thermal "cracking".

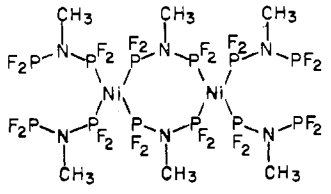


VII



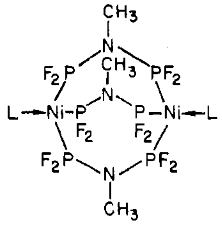
VIII

An intermediate in the formation of $\{[CH_3N(PF_2)_2]_2Ni\}_n$ from $Ni(CO)_4$ and $CH_3N(PF_2)_2$ in a photochemical reaction is a low-melting solid of stoichiometry $[CH_3N(PF_2)_2]_3Ni$. Molecular weight determinations indicate this species to be the dimer $\{[CH_3N(PF_2)]_3Ni\}_2$. The presence of two different types of $CH_3N(PF_2)_2$ ligands is indicated by the presence of two methyl carbon-13 resonances (δ 26.9 and 24.3) and two overlapping phosphorus-31 triplets. Structure IX is suggested for $\{[CH_3N(PF_2)_2]_3Ni\}_2$ which contains two bridging biligate bimetallic and four terminal monoligate monometallic $CH_3N(PF_2)_2$ ligands. Conversion of the bimetallic $\{[CH_3N(PF_2)_2]_3Ni\}_2$ (IX) to the polymeric $\{[CH_3N(PF_2)_2]_2Ni\}_n$ (VIII) can be interpreted as a novel type of coordination polymerization in which the uncoordinated ends of half of the monoligate monometallic $CH_3N(PF_2)_2$ ligands in IX displace the remaining half of the monoligate monometallic $CH_3N(PF_2)_2$ ligands to form new bridges between pairs of nickel atoms.

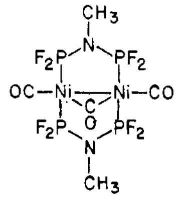


IX

The compounds $\{[CH_3N(PF_2)_2]_3Ni\}_2$ (IX) and $\{[CH_3N(PF_2)_2]_2Ni\}_n$ (VIII) are formed from reactions of $Ni(CO)_4$ with excess $CH_3N(PF_2)_2$. Reactions of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ using limited quantities of $CH_3N(PF_2)_2$ give still different products. Thus, ultraviolet irradiation of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ in molar ratios in the range 1:1 to 2:3 gives the yellow crystalline bimetallic complex $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$. The presence of only one carbon-13 methyl resonance and only one phosphorus-31 NMR triplet for this complex suggests structure X (L = CO) in which all three $CH_3N(PF_2)_2$ bridges are equivalent. The two terminal carbonyl groups in X (L = CO) at opposite ends of the molecule give two closely spaced $\nu(CO)$ frequencies in the infrared spectrum. The proposed structure X (L = CO) for $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ is similar to that determined[25] for the bimetallic cobalt carbonyl complex $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ except for the obvious stereochemical changes associated with removal of the metal–metal bond in going from cobalt to nickel.



X



XI

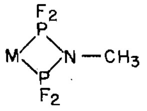
Reaction of equimolar quantities of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ in boiling hexane was found to give a yellow crystalline complex $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ of apparent structure XI similar to reported[26,27] $(bid)_2Ni_2(CO)_3$ complexes (bid = bidentate trivalent phosphorus ligand) such as $[S(P[CF_3]_2)_2]_2Ni_2(CO)_3$, the structure of which has been determined by X-ray crystallography.[28] The infrared spectrum of XI exhibits a $\nu(CO)$ frequency at 1891 cm^{-1} assigned to the bridging carbonyl group in addition to terminal $\nu(CO)$ frequencies at 2070 and 2055 cm^{-1} similar to reported infrared $\nu(CO)$ frequency patterns for related $(bid)_2Ni_2(CO)_3$ complexes. A curious property of yellow $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ is its tendency to become dark red reversibly upon heating above its melting point. A pure dark red species could not be isolated from this pyrolysis product; instead, the dark red material fomed on such heating gradually reverted to yellow $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ upon standing at room temperature.

A characteristic property of the nickel carbonyl complexes $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ (X: L = CO) and $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ (XI) is the facile replacement of their carbonyl groups with donor ligands such as phosphines, phosphites, and isocyanides. Thus, treatment of the dicarbonyl $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ (X: L = CO) with such ligands L (L = $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(C_6H_5)_3P$, $(CH_3)_3CNC$) in hexane at room temperature results in rapid effervescence of CO leading to replacement of both terminal carbonyl groups to give the corresponding white to pale yellow carbonyl-free complexes $[CH_3N(PF_2)_2]_3Ni_2L_2$ (X). Analogous treatment of $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ with excess $CH_3N(PF_2)_2$ at room temperature gives $[CH_3N(PF_2)_2]_5Ni_2$, apparently X (L = monodentate $CH_3N(PF_2)_2$). Heating the tricarbonyl $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ with the trialkyl phosphites $(RO)_3P$

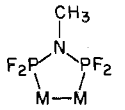
($R = CH_3, C_2H_5$) in boiling hexane also results in formation of the same $[CH_3N(PF_2)_2]_3Ni_2[P(OR)_3]_2$ (X: $L = (RO)_3P$; $R = CH_3, C_2H_5$) derivatives. These latter reactions involve more extensive reorganization of the $[CH_3N(PF_2)_2]_nNi_2$ backbone of the system. The $[CH_3N(PF_2)_2]_3Ni_2L_2$ (X: $L = (CH_3O)_3P, (C_2H_5O)_3P, (C_6H_5)_3P, (CH_3)_3CNC$) derivatives have been characterized not only by elemental analyses but also by their proton NMR spectra, integration of which showed the correct ratios of the L protons to the $CH_3N(PF_2)_2$ protons.

Discussion

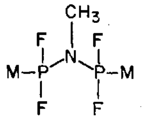
The "bite" of $CH_3N(PF_2)_2$ functioning as a biligate monometallic ligand is small since a four-membered chelate ring (XII) is formed. Thus, the higher the coordination number of the central metal atom, the more likely the $CH_3N(PF_2)_2$ is to function as a biligate monometallic ligand rather than, for example, as a biligate bimetallic ligand as exemplified by XIII or XIV.



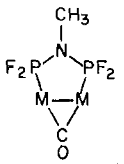
XII



XIII



XIV



XV

The effect of the coordination number of the central metal atom on the preferred coordination type of the $CH_3N(PF_2)_2$ is illustrated very well in the products obtained from reactions of $CH_3N(PF_2)_2$ with the monometallic metal carbonyls discussed in this paper. Thus, the octahedral metal carbonyls $M(CO)_6$ (coordination number six) readily form the biligate monometallic complexes $[CH_3N(PF_2)_2]_3M$ (I: M = Cr, Mo, W), which exhibit exceptional thermal and oxidative stabilities. Reaction of the five-coordinate $Fe(CO)_5$ with $CH_3N(PF_2)_2$ under forcing conditions can be made to give the biligate monometallic derivative $[CH_3N(PF_2)_2]_2FeCO$ (II) but reactions of iron carbonyls with $CH_3N(PF_2)_2$ under most conditions give one or more of the biligate bimetallic iron carbonyl derivatives III, IV, V, and VI. None of the products isolated from the reactions of the four-coordinate $Ni(CO)_4$ with $CH_3N(PF_2)_2$ (VIII, IX, X (L = CO), and XI) appear to contain biligate monometallic $CH_3N(PF_2)_2$ ligands. However, there is mass spectral evidence for the existence in the vapor phase of the dimer $[CH_3N(PF_2)_2]_4Ni_2$ (VII) which is difficult to formulate without biligate monometallic $CH_3N(PF_2)_2$ ligands.

Bimetallic metal carbonyl derivatives of the transition metals of even atomic number involved in this work containing one or more bridging biligate bimetallic $CH_3N(PF_2)_2$ ligands and a metal–metal bond require an odd number of metal carbonyl groups to achieve the favored rare-gas electronic configuration. As a consequence of this requirement, the structural element XV is frequently found in such complexes in which a metal–metal bond is bridged not only by one or two $CH_3N(PF_2)_2$ ligands but also by a single bridging carbonyl group thereby leaving an equal number of carbonyl groups for each metal atom. Compounds of this type discussed in this paper are $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (III), $CH_3N(PF_2)_2Fe_2(CO)_7$ (VI), and $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$ (XI). On the other hand, we have not found any bimetallic compounds in this work containing bridging carbonyl groups without metal–metal bonds even though bridging $CH_3N(PF_2)_2$ ligands in complexes such as $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (IV), $CH_3N(PF_2)_2[Fe(CO)_4]_2$ (V), and $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ (X: L = CO) might be expected to hold two transition metals close enough to allow bridging carbonyls. Apparently for bridging carbonyl groups to be feasible in polymetallic transition-metal derivatives, the two transition metals being bridged must be so close together that formation of a metal–metal bond must also occur.

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Registry No. $[CH_3N(PF_2)_2]_3Cr$, 63404-40-0; $[CH_3N(PF_2)_2]_3Mo$, 63353-75-3; $[CH_3N(PF_2)_2]_3W$, 63371-85-7; $[CH_3N(PF_2)_2]_2FeCO$, 66632-65-3; $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$, 62944-85-8; $[CH_3N(PF_2)_2Fe(CO)_3]_2$, 62944-84-7; $CH_3N(PF_2)_2[Fe(CO)_4]_2$, 62944-86-9; $CH_3N(PF_2)_2Fe_2(CO)_7$, 63138-97-6; $\{[CH_3N(PF_2)_2]_2Ni\}_n$, 66632-67-5; $[CH_3N(PF_2)_2]_6Ni_2$, 66674-79-1; $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$, 66632-77-7; $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$, 66632-76-6; $[CH_3N(PF_2)_2]_3Ni_2[P(OCH_3)_3]_2$, 66632-75-5; $[CH_3N(PF_2)_2]_3Ni_2(P(OC_2H_5)_3]_2$, 66632-74-4; $[CH_3N(PF_2)_2]_3Ni_2[P(C_6H_3)_3]_2$, 66632-73-3; $[CH_3N(PF_2)_2]_3Ni_2[CNC(CH_3)_3]_2$, 66632-72-2; $[CH_3N(PF_2)_2]_5Ni_2$, 66632-82-4; $CH_3N(PCl_2)_2$, 17648-16-7; $CH_3N(PF_2)_2$, 17648-18-9; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; $Fe_2(CO)_9$, 15321-51-4; $Ni(CO)_4$, 13463-39-3.

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